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14. ABSTRACT
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 11 May 2006 through 31 July 2007. This report presents a variant of the Ab Intio Fragment Orbital Theory where the correlation problem in the excited states is addressed in terms of the Coupled Cluster theory at the singles and doubles level. In contrast to the earlier formulations, the present theory includes triple excitations in the excited states and double excitations in the ground state. Moreover, because of the inherent nature of Coupled Cluster techniques, the correlation thus included is size consistent, The present theory is applied to the study of the excites states of polyene chains of various lengths.

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Abstract

We present a variant of the Ab Intio Fragment Orbital Theory where the correlation problem in the excited states is addressed in terms of the Coupled Cluster theory at the singles and doubles level . In contrast to the earlier formulations, the present theory includes triple excitations in the excited states and double excitations in the ground state. Moreover, because of the inherent nature of Coupled Cluster techniques, the correlation thus included is size consistent. The present theory is applied to the study of the excites states of polyene chains of various lengths.

I. Introduction

In several previous reports [1] we have presented a fragmented ab-initio approach, which we have called the Ab Intio Fragment Orbital Theory (AFOT), that consists of treating a given large molecule fragment by fragment. The fragments are chosen as chemically viable units (such as the functional groups), "rectified" by adding hydrogens and then processed via the Hartree-Fock methods to obtain the corresponding occupied and virtual orbitals (called Fragment Molecular Orbitals – "FMO's"). A truncated set of these orbitals near the top of the valence band are chosen as the active FMO's and are used to describe the low-lying excitations. This is accomplished in three steps: First, both for representing the one-electron terms accurately as well as computing the molecular 1- and 2-electron integrals between the nearest and also the next-nearest fragments, new Harteree-Fock calculations are performed on what are called segments. These are built by surrounding each fragment by its nearest neighbors. Secondly, using a Configuration Interaction-Singles (CI-S) procedure, the excited states are generated, which are then corrected by including relaxation terms. The method has been found quite successful for low-lying excited states (where the single excitations from the Hartree-Fock gound state account for most of the excitation). They have also been used successfully to predict optical properties.

In extending the method to organo-metallics (e.g. Pt compounds) [2] it was found, however, that the fragment orbitals as obtained from the fragment calculations are not adequate for acceptable accuracy for the description of the excited states. It is necessary to use instead their corresponding modified forms from their respective segment calculations. Clearly this new situation results from a strong influence of the neighbors on the nature of the active FMO's. Since the FMO's are now essentially derived from the segment calculations, the corresponding 1- and 2- molecular integrals can only be

computed by a second pass of generation of the AO-supermatrices. This, however, increases the AFOT computation times only slightly, since the bulk of the computing time is spent in performing the 4-index transformation involving from AO to FMOs', which step is not altered.

For achieving chemical accuracy in excitation energies, we have to consider two types of corrections to the CI-S states (see above): At the level of the segment calculations, the relaxation corrections are to be evaluated for the non-excited occupied orbitals. These have been successfully carried out in the past by a second–order perturbation approach, using a truncated excitation space. At the global level, where all the active FMO's participate, the relaxation is obtained in terms of single excitations on the CIS states. These are in fact double excitations with respect to the closed-shell H.F. ground state. We do not, however, allow these excitations in the ground state, since these excitations introduce "correlation" in the Hartree-Fock, while they do not on the CI-S excited states.

However, even though in most cases, direct correlation terms do not substantially alter the excitation energy, for low excitation energies they may not be always negligible. In order to include the correlation terms, we have also to ensure that they are size-consistent. This is achieved most elegantly by treating the correlation via the Coupled-Cluster (Singles and Doubles) (CCSD) theory [3-5]. In the AFOT framework, the most important contribution of the CCSD treatment of the correlation takes place at the "global" level of calculations where all the active FMO's are involved. We will therefore restrict the application of CCSD only to the correlation contribution involving the active FMOs'.

We present below a step-by-step description of the above "two-pass" AFOT procedure. We also carry out calculations using the present AFOT procedure on the excited states of trans-polyene chains of various lengths and compare them with other theoretical calculations.

II. Coupled-Cluster Wavefunction and Correlation

The CCSD ansatz for the ground state is as follows:

$$\Psi = \exp(T)|0\rangle \tag{1}$$

where |0> is the Hartree Fock wavefunction and T consists of single and double excitations:

$$T = T_1 + T_2 = \sum_{ia} t_i^a a^+ i + \sum_{i>j;a>b} t_{ij}^{ab} (a^+ i)(b^+ j) \tag{2}$$

where the 't' s are the excitation amplitudes.
These are determined from the corresponding Schroedinger equation

$$H|\Psi\rangle = E_{CC}|\Psi\rangle \tag{3}$$

with

$$\begin{aligned} E_{CC} &= \langle 0|H\exp(T)|0\rangle \\ &= E_{HF} + \sum_{i>j;a>b} \langle ij\|ab\rangle \left(t_{ij}^{ab} - t_i^a t_j^b - t_i^b t_j^a\right) \end{aligned} \tag{3a}$$

Starting from an initial solution

$$t_i^a = 0\,; \quad t_{ij}^{ab} = \frac{\langle ij\|ab\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{4}$$

these amplitudes are determined by the Galerkin's procedure by left-multiplying Eq. (3) by $\langle 0|\, i^+ a$ and $\langle 0|(i^+a)(j^+b)$ and solving the resulting equations iteratively. The starting solutions, Eq. (4), clearly represent the MP2 approximation in an MBPT approach.

In describing the excited states, we shall follow the CCSD equation of motion approach as proposed by Bartlett and coworkers with some modification. We assume the zero-th order excited state wavefunction in the form:

$$|\Psi_{ex}^{(0)}\rangle = \sum_{\mu} A_\mu |\mu\rangle \tag{5}$$

where $|\mu\rangle$ is an excitation determinant or a spin-symmetrized combination of several determinants. The corresponding CCSD wavefunction is given by

$$|\Psi_{ex}\rangle = \exp(T)|\Psi_{ex}^{(0)}\rangle \tag{6}$$

The total CCSD energy is given by:

$$E = \sum_{\mu,\nu} A_\mu \overline{H}_{\mu\nu} A_\nu \tag{7}$$

where H is given by:

$$\overline{H} = H + [H,T] + \tfrac{1}{2}[[H,T],T] + \tfrac{1}{6}[[[H,T],T],T] + \tfrac{1}{24}[[[[H,T],T],T],T] \tag{8}$$

In the method followed by Bartlett et al [3,4] the t-amplitudes are frozen at the values obtained for the G.S. We would like to depart from this choice by arguing that while the non-zero values of T_1 result only because of the breakdown of the Koopman's theorem

caused by the presence of the double excitation terms in the G.S., they are largely determined by the relaxation of the orbitals going from the G.S. to the excited state wavefunctions represented by Eq. (5). We solve for these T_1 amplitudes as follows:

$$t_{ia}^{(1)} = \frac{\left\langle a^+ i\Psi_{ex}^{(0)} \middle| H \middle| \Psi_{ex}^{(0)} \right\rangle}{\left\langle a^+ i\Psi_{ex}^{(0)} \middle| H \middle| a^+ i\Psi_{ex}^{(0)} \right\rangle} \tag{9}$$

We shall take the second-order, T_2 coefficients as

$$t_{ij;ab}^{(2)} = \frac{\left\langle (ia)(jb) \middle\| i^2 j^2 \right\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{10}$$

The correlation-relaxation contribution will be calculated from Eq.

$$\Delta E = \sum A_\mu A_\nu \left[\left\langle \mu \middle| \overline{H} \middle| \nu \right\rangle - \left\langle \mu \middle| H \middle| \nu \right\rangle \right] \tag{11}$$

Considering the fact that $\Psi_{ex}^{(0)}$ consists only of single excitations from the Hartree-Fock, one can easily simplify the above expression to

$$\Delta E = \sum A_\mu A_\nu \Delta H_{\mu\nu} \tag{12}$$

$$\Delta H_{\mu\nu} = \left\langle \mu \middle| HT - TH + \tfrac{1}{2}\left(HT_1^2 - 2T_1 HT_1 \right) \middle| \nu \right\rangle \tag{12a}$$

III. The Present Architecture of the AFOT Procedure

(a).The present AFOT code is an add-on to the GAMESS 2004 version with the "control" part of the GAMESS input retained intact. With the "AFOT" keyword on, the program reads in the input for the geometry in a slightly different format (see below).

(b) Before inputting the geometry, the number of active FMOs' (n_{val} , n_{vir}) are specified. The geometry is given in terms of fragments separated by a $ sign. It is implied that none of the fragments have common atoms.

(c) The open-shell ROHF wavefunctions of the distinct atoms in their appropriate valence states are obtained and the corresponding occupied and virtuals orbitals are saved in the RAM.

(d) Attach rectification hydrogen atoms to the fragments to tie off the dangling orbitals. Form the initial orbitals by using the information from (c). Obtain the RHF ground states for each fragment and save the resulting occupied and unoccupied orbitals in the virtual memory.

(e) Surround each of the fragments by its nearest neighbors, with the latter rectified by hydrogens. The resulting closed-shell molecule is called a segment. These segments are now treated with the RHF procedure. The starting input orbitals are constructed by including all the occupied orbitals of the constituent fragments except those that correspond to the orbitals that bond the rectification hydrogen atoms to be eliminated in juxtaposing the neighboring fragments in forming the segments. These are replaced by what we have termed the link orbitals obtained separately by diatomic calculations. The unoccupied orbitals of the fragments are the stacked up on top of the occupied ones. The resulting FMO's constitute the total MO-expansion basis of the segment. Before they are used in solving the segment Fock equation, they are symmetrically orthonormalized (not Schmidt orthonormalized) so they remain identified as belonging to their original fragments on equal footings.

(f) Upon the convergence of the RHF process and the generation of the segment canonical orbitals, the active FMO's (AFMO) localized in the central fragment (defined as the fragment(s) that are not linked to any rectification hydrogen atom) are then derived as follows: We expand the anticipated FMO in terms of the non-core orbitals (both occupied and virtual) of the central fragment in question by a least square fitting process by minimizing

$$L = \int (\sum_{i \subset A} a_i \phi_i - \sum_{i \subset C} b_i \chi_i)^2 d\vec{r} \tag{13}$$

where {A} represent the space of the active MO's of the segment and {C} represent the part of the non-core orbitals, associated with the central fragment of interest. Both the 'a's and the 'b's are varied in the least square-fitting process. This yields the optimal active occupied FMO's for the central fragment. We obtain the excited FMO's as follows. Let ϕ_{oc} denote the highest occupied AFMO. The corresponding ϕ_{ex} is determined by minimizing the single-excitation energy:

$$\Delta E_{ex} = \varepsilon_{ex} - \varepsilon_{oc} - J_{ex,oc} + 2K_{ex,oc} \tag{14}$$

This amounts to solving the excited Fock equation:

$$(F_0 - \mathcal{J}_{oo} + 2\,\mathcal{K}_{oo})\phi_{ex} = \varepsilon\,\phi_{ex} \tag{15}$$

where ϕ_{ex} is expanded in terms of the unoccupied space of the central fragment, $\mathcal{J}_{oo}$, $\mathcal{K}_{oo}$ being the Coulomb and exchange operators. If it is desired to have multiple excited orbitals $\phi_{ex,}$ higher roots of the same equation are selected.

The above AFMO's along with the RHF Fock matrix of the segment are now saved.

(g) Upon completion of all the segment calculations, we revisit each one of them (in the same sequence) in the "second" pass of the calculations. We recall the appropriate Fock matrix and all the AFMO's pertaining to all the fragments of the segment in question. Consider the total energy resulting from excitation of one of the occupied AFMO's of the central fragment ϕ_i to one of the excited orbitals ϕ_k belonging to any of the fragments (central or otherwise):

$$\Delta E_{ik} = E_0 + \varepsilon_k - \varepsilon_i - J_{ik} + 2K_{ik} \qquad (14)$$

The contribution from the relaxation of all the occupied orbitals except ϕ_i is given by the second order perturbation expression:

$$\Delta E_{relax,ik} = -\sum_{j,l} \frac{< l|\mathcal{J}_k - \mathcal{J}_i - (\mathcal{K}_k - \mathcal{K}_i)/2|j >^2}{\varepsilon_k - \varepsilon_i} \qquad (15)$$

where j goes over the occupied space excepting i and l goes over different parts of the unoccupied space; for j representing core orbitals, the whole unoccupied space is used while for the valence orbitals, the unoccupied space excludes all the excited AFMO's.

These relaxation contributions are saved for the future global calculations (see below). We also compute and save the 1- and 2-el AFMO integrals, $F_{0,pq}$ and I_{pqrs} , over the AFMO's p,q,r,s.

(h) Finally, the "global" calculations, which lead to the total molecular excited states as well as the optical properties, are carried out. First we have to evaluate both the 2-el integrals as well as the relaxation contributions that are not already calculated at the segment level. In this work, we employ the simplest electrostatic approximation for the 2-electron integrals:

$$I_{pqrs} = S_{pq}S_{rs}/R_{pqrs} \qquad (16)$$

where R_{pqrs} is the 'average' distance between the overlap pq and rs.

The relaxation contributions for "distant" charge transfers are found by extrapolation.

The first step in global calculations is to recall the saved 1- and 2-el integrals as well as the relaxation contributions and carry out a configuration interaction (singles) (CIS) calculation. All single excitations within the active FMO space are included. Next we compute the relaxation contributions for a CIS-state of interest a s given by

$$\Delta E_{relax} = -\Sigma\, A_{ik}^2 \Delta E_{relax,ik} \qquad (17)$$

where A_{ik} is the CI-coefficient for the single excitation i→k. This is followed by a CCSD calculation yielding the contributions of the singles and double excitations on the CIS states.

IV. Calculations, Results and Discussion

We employ the above formalism to the study of the excited states (particularly the 1^1B_u state) of the trans-polyene systems $C_{2n}H_{2n+2}$, n=1,10. The basis set chosen for all of our calculations reported in this work is the Gaussian '6-31' set. In Table I we summarize the results. We present the results for the 2^1A_g state (which lies consistently higher than the Bu state because of the absence of any 'triple-triple' excitations in our calculations) to indicate the narrowing of the 2^1Ag-1^1B_u gap. The correlation (resulting from MP2-lecel double excitations on both ground state and the excited state ($1B_u$)) seems to cancel out routinely for all sizes of polyene systems considered. The contribution from the 'relaxation terms' at the global level seems to be negligibly small. We must, however, note that this observation pertains only to the global level, namely involving the homo-lumo orbitals. There is considerable relaxation contribution at the segment level (of the order of 1-2 eV) from the core orbitals (see discussion above).

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Table I. The calculated 1^1B_u and 2^1A_g energies for various size polyenes

Polyenes	1^1B_u Energy (eV)	ΔE_{MP2} (eV)	ΔE_{CCSD} (eV)	2^1A_g Energy (eV)
C_8H_{10}	4.46	<.001	.08	6.07
$C_{12}H_{14}$	3.74	.001	.11	4.23
$C_{16}H_{18}$	3.62	.001	.12	4.01
$C_{20}H_{22}$	3.55	.001	.12	3.93